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Chlorometallate and palladium cluster complexes of wide-span diimine and diamine ligands**

John S. Hart,[1] Simon Parsons[1] and Jason B. Love[1,*]

[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[*]Corresponding author; e-mail: jason.love@ed.ac.uk, fax: (+) 44 131 6504743

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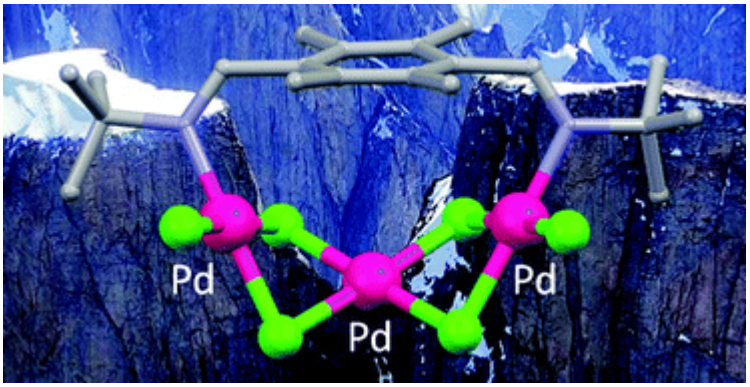
Graphical abstract:



Keywords:
organometallic oxides; crystal-structure; reduction; macrocycle; mechanism; design; anions

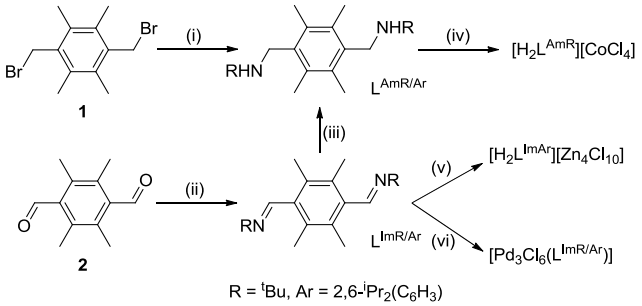
Abstract

Diimine and diamine ligands that are unable to coordinate to a single metal favour the formation of unusual, high-nuclearity Zn chlorometallate and palladium chloride complexes.

Introduction

Ligands that can promote the assembly of multiple metal cations into precisely-structured arrangements are highly desirable as these multimetallic motifs impact on a diverse range of chemical topics such as catalysis,[1] bio-inorganic chemistry,[2] medicine,[3] and single molecule magnetism.[4] In particular, ligand designs incorporating 1,4-disubstituted arenes have been intensively investigated as platforms that favour bi- and multinuclear complex formation due to the inability of the two donors to chelate to a single metal cation.[5] For example, imine and amine acyclic ligands,[6] marocycles,[7] and cryptands[8] dervied from 1,4-disubstituted arenes have been developed and show a propensity to form polynuclear complexes, although in simple systems cyclometallation reactions at the central aryl ring are observed, particularly with late transition metals.[9]

We are interested in developing straightforwardly-synthesised and inexpensive ligands for the assembly of multinuclear complexes of metals from across the Periodic Table,[10] in particular to access new chemistry that can occur within well-defined cavities such as found in Pacman complexes,[11] and related supramolecular assemblies.[12] We report here on the use of new wide-span diimine and diamine ligands as outer and inner-sphere coordination platforms for the generation of new, high-nuclearity chlorometallate and palladium chloride complexes. The use of durene in the ligand design ensures that undesired cyclometallation reactions are minimised.



Scheme 1. Synthesis of wide-span diimine (L^{Im}) and diamine (L^{Am}) ligands and their chlorometallate and cluster complexes. Reagents and conditions: (i) H_2NR/Ar, MeCN; (ii) H_2NR/Ar, MeCN; (iii) $NaBH_4$, MeOH, R = ^{t}Bu; (iv) 2 HCl, Et_2O, $CoCl_2$; (v) 2 HCl, Et_2O, 4 $ZnCl_2$; (vi) 3 $PdCl_2(MeCN)_2$, CH_2Cl_2.

The pro-ligands L^{Im} and L^{Am} were synthesised in high yield from the readily available precursors **1** and **2** through straightforward bromide substitution and Schiff-base condensation routes, respectively (Scheme 1). Borohydride reduction of diimine L^{ImR} proved to be the most reproducible route to diamine L^{AmR}. The 2,6-diisopropylaryl-substituted diimine L^{ImAr} and diamine L^{AmAr} compounds were crystallised from saturated solutions of MeCN and their X-ray crystal structures determined (Fig. 1). In the solid state, both L^{ImAr} and L^{AmAr} form extended structures through intermolecular hydrogen-bonding interactions and display no solvent incorporation. In L^{ImAr} (Fig. 1, top), the imine N1-C13 bonds (1.236(2) Å) adopt an anti-conformation (torsion angle = 180.0(2)^o) and are offset by 29.8(3)^o with respect to the central aryl ring. The sterically-demanding ^{i}Pr substituents on the terminal aryl groups result in an approximately orthogonal orientation (72.7(2)^o) of this aryl ring to the imine N=C group. This orientation results in an intermolecular interaction between the C10 isopropyl methyl hydrogens and the central aryl ring (C10···C16 = 3.745(4) Å), so forming a chain motif in the extended structure. Reduction of the N=C double bond in L^{ImAr} to form L^{AmAr} allows free rotation around the N1-C13 single bond (1.489(2) Å) and results in a different structure in the solid state (Fig. 1, bottom) in which the N1-C13 bonds adopt a syn-conformation (torsion angles = 79.9(2)/84.0(2)^o). As with L^{ImAr}, the steric demand of the ^{i}Pr$_2$(C$_6$H$_3$) substituent results in an approximately orthogonal orientation of this group in relation to the amine N1-C13 bond (76.1(2)/68.2(2)^o), but in this case the presence of the amino hydrogen results in a hydrogen bond between the two amines (N1···N1' = 3.264(2) Å); π-H interactions are also seen in the extended structure.

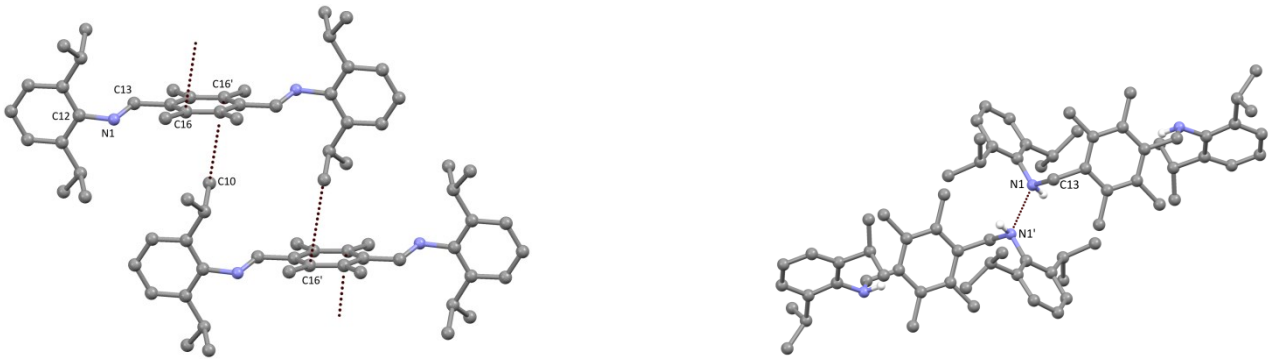


Figure 1. Ball and stick representations of the X-ray crystal structures of diimine L^{ImAr} (left) and diamine L^{AmAr} (right). For clarity, all hydrogen atoms except those involved in hydrogen bonding are omitted.

The coordination chemistry of these ligands was investigated (Scheme 1). Reactions between L^{Im} or L^{Am} and either $CoCl_2$ or $ZnCl_2$ in THF showed little change in the resonances for L in the ^{1}H NMR spectra. However, the use of $CDCl_3$ as the NMR solvent resulted in the crystallisation of the chlorometallate salts $[H_2L^{AmR}][CoCl_4]$ and $[H_2L^{ImAr}][Zn_4Cl_{10}]$, presumably as a result of the presence of adventitious HCl in

$CDCl_3$. Scaled-up reactions were carried out in which the ligands were protonated by HCl (2 eq) in Et_2O prior to the addition of $CoCl_2$ (1 eq) or $ZnCl_2$ (4 eq) in Et_2O. This latter procedure resulted in the formation of analytically pure materials. The X-ray crystal structures of both $[H_2L^{AmR}][CoCl_4]$ and $[H_2L^{ImAr}][Zn_4Cl_{10}]$ were determined (Fig. 2) and show that the protonated ligands interact with the chlorometallate salts through a series of hydrogen-bonding interactions; all hydrogens involved in hydrogen-bonding were located in the difference Fourier map and refined with riding thermal parameters and bond distance restraints.

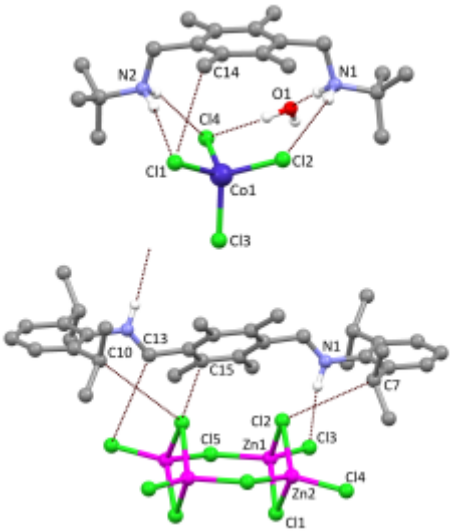


Figure 2. Ball and stick representations of the X-ray crystal structures of $[H_2L^{AmR}][CoCl_4](H_2O)(CHCl_3)$ (top) and $[H_2L^{ImAr}][Zn_4Cl_{10}]$ (bottom). For clarity, $CHCl_3$ solvent of crystallisation and all hydrogen atoms except those involved in hydrogen bonding are omitted.

In the solid state structure of $[H_2L^{AmR}][CoCl_4]$ (Fig 2., top) the amine appendages adopt a syn-conformation (torsion angle = 6.5(3)°) that results in a hydrogen-bonded cavity suited for chlorometallate recognition (over chloride), with N-H···Cl and C-H···Cl hydrogen-bonding interactions ranging in distance from 3.165(3) to 3.357(3) Å. The chelation of the cobaltate anion by the wide-span ligand causes some strain, as evidenced by the 10° curvature of the central diaminoarene and the inclusion of a molecule of water that interacts both with the protonated amine (N1···O1 2.817(5) Å) and the cobaltate (Cl4···O1 3.165(3) Å); as with the free ligands above, other intra- and intermolecular close contacts (to $CHCl_3$ solvent of crystallisation) are present in the extended structure.

In the solid state structure of $[H_2L^{ImAr}][Zn_4Cl_{10}]$ (Fig. 2, bottom), the protonated imine arms adopt an anti-conformation (torsion angle = 176.0(2)°) and the terminal aryl groups, and to a lesser extent the

central arene, are oriented-orthogonally to the N=C bond (torsion angles = 88.1(3) and 53.4(4)°, respectively). As with the cobaltate above, a variety of weak interactions exist between the doubly-protonated diimine and the zincate, with N-H···Cl and C-H···Cl hydrogen bonding interactings ranging in distance from 3.152(3) to 3.759(3) Å. However, in this case, the wide-span ligand framework has favoured the isolation of an unusual $Zn_4Cl_{10}^{2-}$ anionic cluster. In this cluster, each zinc cation is tetrahedral with one terminal chloride and three chlorides bridging to adjacent zinc cations. This results in a rectangular arrangement of zinc cations in which two opposing sides of the rectangle comprise either a single bridging chloride or two bridging chlorides, with Zn···Zn distances of 3.8345(5) Å and 3.1405(5) Å and Zn-Cl-Zn angles of 114.25(3) and 85.30(2)°. Also, the anti-conformation of the imines allows for an intermolecular N1···Cl3 hydrogen bond (3.152(3) Å) from which a linear chain of alternately sandwiched ligand and metallate clusters grows. While $Zn_4Cl_{10}^{2-}$ anionic clusters have been observed before, to our knowledge they adopt adamantane or open-chain structural motifs and not the new rectangular arrangement of Zn cations seen here.[13] Furthermore, metal chloride clusters that adopt a similar structural motif are rare, and limited primarily to *o*-phenylene-metallated Pt_4 chlorides,[14] $Mo_4Cl_{12}^{3-}$ clusters,[15] and the chlorobismuthate and antimonates $M_4Cl_{18}^{6-}$ (M = Bi, Sb).[16] Significantly, the recognition of high-nuclearity chlorometallates by L^{Im} and L^{Am} may impact on the high-efficiency, hydrometallurgical extraction of base and precious metals.[17]

The reaction between $PdCl_2(MeCN)_2$ and either L^{ImAr} or L^{ImR} in CH_2Cl_2 led to the sole formation of the trinuclear palladium chloride cluster $[Pd_3Cl_6(L)]$; this formulation was supported by elemental analysis. The X-ray crystal structures of $[Pd_3Cl_6(L^{ImAr})]$ and $[Pd_3Cl_6(L^{ImR})]$ were determined (Fig. 3) and were found to be isostructural; as such, only the former structure will be discussed (Fig.3, top). In a similar manner to $[H_2L^{AmR}][CoCl_4]$, the imine appendages adopt a syn-conformation (torsion angle = 6(2)°) that allows the ligand to chelate to the single Pd_3Cl_6 cluster through the imine nitrogens N1 and N2. Also, the terminal and central aryl rings are similarly tilted with respect to the N=C bond by 67(4) and 73(4)°, respectively. Each Pd cation is square planar but the Pd_3Cl_6 cluster is not linear due to the constraints imposed by the chelating diimine ligand. This feature results in a cradle arrangement in which the Pd1-Pd2-Pd3 angle is 127.4(4)° with Pd(μ-Cl)Pd angles of approximately 90°.

The solid state structure of $[Pd_3Cl_6(L^{ImAr})]$ is retained in solution. In the ^1H NMR spectrum (Fig. S1, Supplementary information), only one imine resonance is seen at 8.38 ppm, whereas two distinct CH_3 environments are seen at 3.75 and 2.09 ppm for the central arene, which reflects the asymmetry of binding to the Pd_3Cl_6 cluster. Furthermore, free rotation about the N-C bond for the terminal 2,6-diisopropyl aryl substituent is hindered, as reflected by the presence of two isopropyl CH resonances at 3.56 and 3.49 ppm and four resonances for the CH_3 environments. The ^1H NMR spectrum of $[Pd_3Cl_6(L^{ImR})]$ is similar (Fig. S2), indicating that the solid state structure of this complex is also retained in solution, but shows only one resonance for the ^{t}Bu substituent at 1.22 ppm. Furthermore, the ESI mass

spectrum of $[Pd_3Cl_6(L^{ImR})]$ shows an ion at *m/z* 682 for the partially-intact cluster $[Pd_3Cl_5(L^{ImR})]^+$, and indicates structural retention in solution.

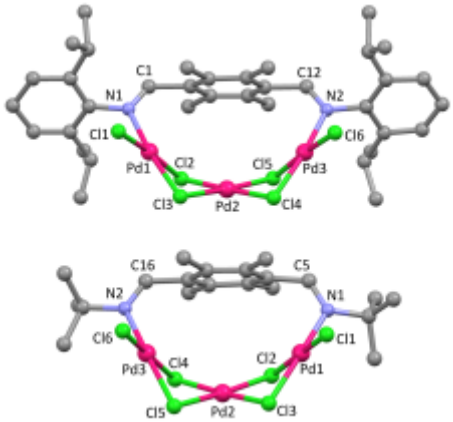


Figure 3. Ball and stick representations of the X-ray crystal structures of $[Pd_3Cl_6(L^{ImAr})]$ and $[Pd_3Cl_6(L^{ImR})]$. For clarity, disorder components, solvent of crystallisation, and all hydrogen atoms are omitted.

High nuclearity complexes of Pd chloride are rare and the $[Pd_3Cl_6(L)]$ complexes can be viewed as short fragments of polymeric $(PdCl_2)_n$. While postulated through indirect evidence,[18] only a single example of the crystallographic characterisation of a $PdCl_2$ trimer end-capped by organic ligands has been described;[19] in this example, the unusual Pd_3Cl_6 motif was stabilised through the use of a large cone-angled, bowl-shaped triarylphosphine. Trinuclear PdCl structures are also known for allyl-complexes, although in these cases one chloride has been substituted by the allyl ligand.[20] The related dianion $Pd_3Cl_8^{2-}$ has also been characterised structurally as its Bu_4N ammonium salt.[21] In all of these previous structures, the Pd_3Cl_6 motif is linear, in contrast to the cradle structure seen by us in $[Pd_3Cl_6(L)]$. Presumably, this new bent geometry for the Pd_3Cl_6 cluster is necessary to allow a good fit to the wide-span diimine ligands. Furthermore, it is evident that methyl substitution of the central arene ligand has ensured that the formation of cyclometallated products is inhibited.

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